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Theoretical study of fullerene (C60) force field at room temperature

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Abstract

In this work we have studied the potential energy of the fullerene molecule which is an organic semiconductor. In this context, the stretching, the bending, the torsion energy and The Van der Waals energy are investigated carefully. The best state of charge carrier's transport is when energy becomes maximal. So, the stretching energy takes the value 6.13 eV, the bending energy takes the values 11.24 eV and 1.25 eV and the torsion energy takes the value 0.35 eV. Our results are in a good agreement with those extracted from literature.

Peer-review under responsibility of the Euro-Mediterranean Institute for Sustainable Development (EUMISD)

Keywords: Organic semi-conductor, Fullerene, force field, photovoltaic;

1. Introduction

In recent years, fullerene derivatives have become an important group of organic semiconductors, which they have found uses in solar cells [1], thin film transistors [2], and photo-detectors [3].

The concept of fullerene (C60) was first hypothesized in 1970s by *Eiji Osawa*, and observed experimentally in 1985 [4-5]. C60 is a spherical hollow molecule with a diameter of 0.7 nm possessing the highest degree of symmetry of all known molecules. It is made up of 60 *sp2*-hybridized carbon atoms to give rise to a very stable species of a hollow polygon with 60 vertices and 32 faces, which appear as a football [5] as shown in figure 1.

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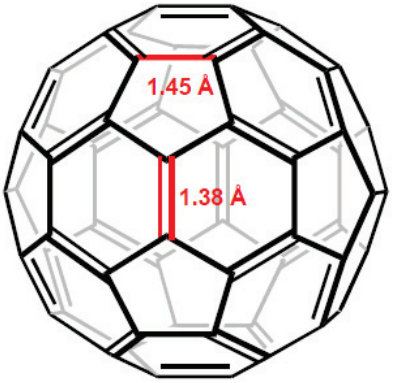

Fig. 1. Fullerene molecule at room temperature with double bond (1.38 A) and single bond (1.45 A) [6].

The pentagonal structures contain the single bonds, and the bridging bonds between pentagonal structures contain the double bonds [7].

As the atoms approach one another, their 2*sp* orbital's begin to overlap. Each electron can then occupy the space around both atoms. In other words, the electrons can be shared by the atoms. The electrons are attracted simultaneously by the positive charges of the two carbon nuclei. This attraction bonds of electrons to both nuclei is the force holding the atoms together. The force that holds the atoms together can still be regarded as arising from the attraction of oppositely charged particles: nuclei and electrons.

In the first hand and in order to understand the charge-carrier transport properties in organic semiconductors we need both the micro- and macroscopic views, and any model combines these views [8]. In the other hand, to calculate charge carrier mobility is the generation of a realistic representation of the position of the atoms in the molecules of the organic semiconductors [9]. The atom's position determines the energy potential (force field) that is governing the transport of charge carrier. So, the first step in the microscopic view determines the potential energy (our study) of molecules.

2. Theoretical model

The force field energy as present in the equation (1) is a sum of those terms, each describing the energy required for distorting a molecule in a specific shape [10].

$$E = \sum_{n_1} E_S + \sum_{n_2} E_B + \sum_{n_3} E_T + \sum_{n_4} E_{vdw} \quad (1)$$

where, E_S is the *stretching* energy between two atoms, E_B represents the *bending* energy, E_T is the *torsion* energy for rotation around a bond and E_{vdw} describe the *non-bonded* atom–atom interactions. n_1, n_2, and n_3 run over all covalently bonded pairs, all bond angles, and all torsion angles, respectively, and n_4 run over all the non-bonded distance. These forces are illustrated in figure 2.

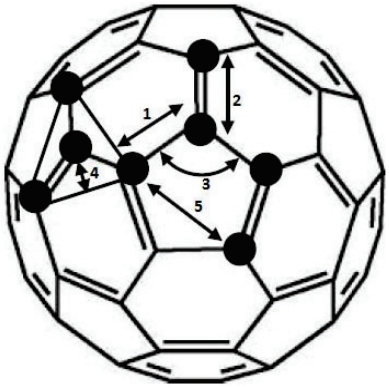

Fig. 2. Illustration of the fundamental force field energy terms. 1 and 2: stretch, 3: bend, 4: torsion, 5: non-bonded.

2.1. Stretching energy

The model bond deformations that exceed very small fluctuations about equilibrium states was discovered by P.M. Morse [11] which can be considered as "strain" terms that model small-scale deviations about reference values. This energy is given in equation 2:

$$E_s = E_0 \left(\left\{ 1 - exp\left[-\beta \left(r_{ij} - r_0 \right) \right] \right\}^2 - 1 \right) \tag{2}$$

with r_{ij} is the actual bond length and r_0 is the equilibrium bond length. E_0 is the bond energy and β^{-1} is the width of the energy.

2.2. Bending energy

It is formed by three bond atoms. The bond angle arrangement around each atom in a molecule is governed by the hybridization of orbitals around the atom. The equation (3) presents this energy [10]:

$$E_B = \frac{1}{2} k_\theta \left(cos\theta_{ijk} - cos\theta_0 \right)^2 \tag{3}$$

Where θ_{ijk} is the angle between the *i*– *j* and *j*–*k* bonds, θ_0 is the equilibrium bond angle, and k_θ is the bending force constant.

2.3. Torsion energy

This energy describes the energy change associated with rotation around a bond with a four-atom sequence, as shown in Figure 2. The torsion potential is written as in equation (4) [10]:

$$E_T = \frac{1}{2} k_\varphi \left(1 - cos\ 2\phi_{ijk} \right) \tag{4}$$

The angle ϕ_{ijk} takes values in the range of [0°, 360°] or [−180°, 180°].

2.4. Van Der Waals energy

The Van Der Waals energy is describing the repulsion or attraction between atoms that are not directly bonded. It may be interpreted as the non-polar part of the interaction not related to the electrostatic energy due to charges.

This energy can be written as present in the equation (5) [11]:

$$E_{vdw} = \epsilon \left[\left(\frac{\sigma}{d_{ij}} \right)^{12} - 2 \left(\frac{\sigma}{d_{ij}} \right)^{6} \right] \quad (5)$$

here σ is the minimum energy distance, ε is the depth of this minimum and d_{ij} is non-bonded distance.

3. Results and discussions

In this section we study the potential energy, which it is necessary to use a harmonic term to describe variations in bond lengths and angles. Consequently, for this work, we employ a force field with stretching, bending, torsion [12] and the van der Waals (Lennard-Jones 12-6) energy [13].

Table 1 summarizes the obtained force constants used in the potential energy of the fullerene C60.

Table 1. The parameters of the C60 potential energies: E_0, β, and r_0 are related to the bond-stretching term, k_θ and θ_0 describe the bond-bending contribution, k_ϕ is the torsion force constant and σ and ϵ are the van der Waals potential constant [10, 14].

Quantity	Value
E_0	6.1322 eV
β	1.8502 A^{-1}
r_0	1.4322 A
k_θ	10 eV
θ_0	120^o
k_ϕ	0.346 eV
σ	3.4681 A^{-1}
ϵ	0.0115 eV

It is interesting to see how the stretching and bending energy of the atoms changes as they approach and then bond. We can see this energy effect in figure 3 (a) and (b). As the atoms approach (moving from right to left on the energy curves), the stretching energy gets strong and stronger (figure 3 (a)), however the bending energy gets lower and lower (figure 3 (b)). Eventually, as the atoms get close enough, the repulsion of the positive charges on the nuclei becomes stronger than the attraction of electrons for nuclei. In other words, the bending energy reaches a minimum value at 120^o (*the equilibrium bond angle* of C-C-C) and then increases, however in the stretching energy reach maximum (6.13 eV) at 1.4322 A (*the equilibrium bond length* of C-C). The distance between nuclei at this maximum energy is the normal distance and the angle between nuclei at this minimum energy is the normal angle between nuclei in the molecule.

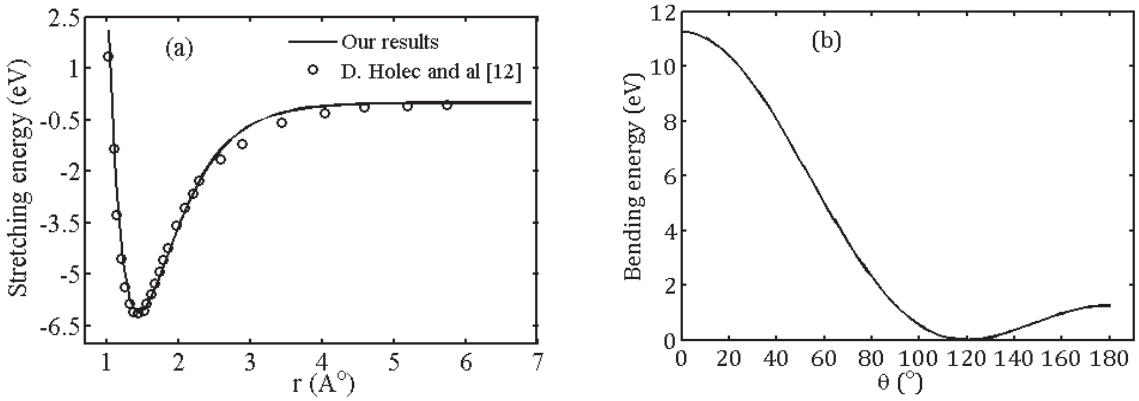

Fig. 3. Stretching energy versus bond length (a) compared with those extracted from [12] and bending energy (b) of C60.

The torsion energy is fundamentally different from the stretching energy and the bond-angle potentials in three aspects:

- The torsion energy function must be periodic in the angle ϕ_{ijk} (Figure 4): if the bond is rotated 180° the energy should return to the same value.
- The torsion energy is low.

The torsion energy takes a maximum value about 0.35 eV at the angles $\phi = 90 + n180$ which n = 0, 1, where the charge carriers in the best state energy for transport. And it takes zero energy at the angles $\phi_{ijk} = n180$ which n = 0, 1, 2.

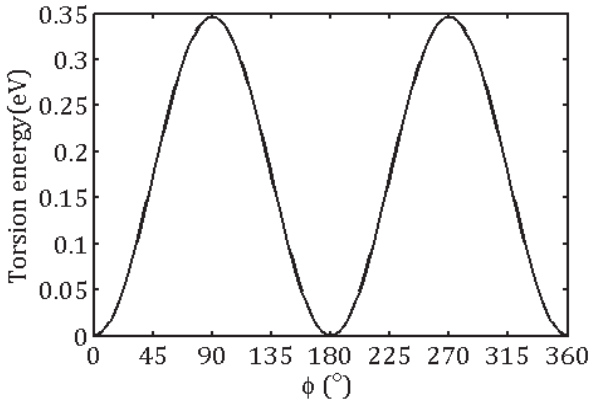

Fig. 4. Torsion energy of C60.

The potential energy curve for two non-bonded atoms is shown in Figure 5. These interactions help to determine the overall conformation of a molecular system.

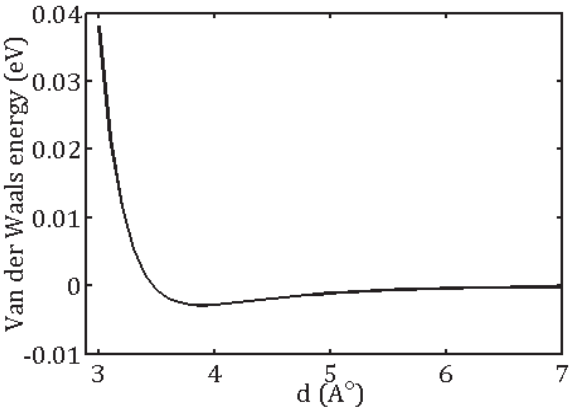

Fig.5. The van Der Waals energy of C60.

The van der Waals energy is zero at large inter-atomic distances and becomes very repulsive for short distances. In quantum mechanical terms, the latter is due to the overlap of the electron clouds of the two atoms, as the negatively charged electrons repel each other. At intermediate distances, there is a slight attraction between two such electron clouds from induced dipole–dipole interactions, physically due to electron correlation.

4. Conclusion

The study of fullerene potential energy has an important effect on the control of charge carrier's transport. As we have already seen the stretching energy and angle bond energy have approximately similar behavior. A rotational barrier has contributions in the non-bonded (van der Waals) terms. So, the knowledge and determine of the force field energy, allow us to find the path and the velocity of charge carriers which controls the mobility. In our perspective, we will develop a Monte-Carlo approach to propagate charges in molecular systems based on the Marcus hopping regime.

Acknowledgements

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